

PATENT SPECIFICATION



879,265

Inventors: NORMAN FLETCHER, JAMES ERIC McINTYRE and
DUNCAN MACLEAN

Date of filing Complete Specification (under Section 3 (3) of the
Patents Act 1949): October 2, 1959

Application Date: October 8, 1958.

No. 32075/58

Application Date: January 26, 1959.

No. 2754/59

Complete Specification Published: October 11, 1961

Index at Acceptance:—Classes 2(5), R3(C6:D1:D2A:D2C:D4:D6:D11:D13:F); and 2(3),
C3A13(A1A1:A1C:C2A:C9:C10E:C10H).

International Classification:—C08g, C07g.

COMPLETE SPECIFICATION

NO DRAWINGS

Manufacture of Highly Polymeric Polymethylene Terephthalates

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved method for the manufacture of filament and film forming polyesters, more particularly to an improved catalytic system for use in the manufacture of highly polymeric polymethylene terephthalate.

In the commercial manufacture of highly polymeric polymethylene terephthalates, it is common practice to use as the starting materials a dialkyl terephthalate and a glycol. These two materials are first subjected to an ester-interchange reaction in the presence of an ester-interchange catalyst and the resulting product is then polycondensed without the removal of the ester-interchange catalyst, which may assist also in the polycondensation stage, or in the presence of a substance added to the reaction mixture for the purpose of catalysing the polycondensation reaction.

For the ester-interchange step many catalysts have been disclosed in the prior art. In some cases catalysts which are excellent for the ester-interchange reaction, such as catalytic compounds containing alkaline earth metals, which group of metals consists of calcium, magnesium, strontium and barium, if allowed to remain in active form during the polycondensation stage, tend to promote colour formation, particularly as regards yellowness and/or they produce insoluble precipitates in the final polyester, both of which conditions result in undesirable effects in filaments, films and the like produced from these polyesters. A process

of this type is disclosed in United States Specification 2739957, in which a calcium compound is used as the ester-interchange catalyst and an antimony compound in combination with a calcium compound, is used as the polycondensation system. The polyesters obtained using this catalyst system as exemplified in the specification, are pale green in colour.

In order to overcome this colour formation and/or insoluble precipitate formation it has been proposed, as for example in British Patent Specification 802921, to inactivate the catalytic metal used in the ester-interchange reaction, prior to polycondensation stage, by the addition of a phosphorus compound at the end of the ester-interchange reaction. By this means a phosphorus acid salt of the alkaline earth metal present is obtained, which is inert catalytically to the polycondensation reaction and which salt is soluble in the final polyester.

In the process of British Specification 802921 it is stated that it is preferred to use an antimony compound as the polycondensation catalyst, and this has commonly been antimony trioxide. Even using this preferred catalyst system it has been found that the resulting polyesters, although of greatly improved colour over those obtained by prior art methods, still contain a noticeable degree of yellowness.

We have now found that when an alkaline earth metal compound is used as an ester-interchange catalyst and is inactivated prior to the polycondensation stage, and the polycondensation catalyst used is a pentavalent compound of antimony, the resulting polyesters exhibit a lower degree of yellowness than do the polyesters obtained using the corresponding trivalent antimony compound, as used in the prior art.

According to the present invention we

provide in a process for the manufacture of highly polymeric polymethylene terephthalates by reacting a dialkyl ester of terephthalic acid with glycol of the series
5 $\text{HO}(\text{CH}_2)_n\text{OH}$, where n is greater than 1 but not exceeding 10, in the presence of a catalytic amount of an alkaline earth metal compound and converting the alkaline earth metal, prior to polycondensing the ester-
10 interchange product, wholly or in part, to a phosphorus containing compound of that metal, which is catalytically inert, the improvement comprising polycondensing in the presence of a catalytic amount of a penta-
15 valent antimony compound.

We have found that of the alkaline earth metal containing compounds used as ester-interchange catalysts in the process of our invention, the catalytic compounds contain-
20 ing magnesium or calcium result in the formation of polyesters exhibiting the lowest degrees of yellowness and at the same time exhibiting the highest degrees of luminance. These factors are commonly held to be
25 criteria of considerable importance in the manufacture of filament and film-forming polyesters. However, any catalytic alkaline earth metal compound is suitable in the process of our invention as the ester-interchange
30 catalyst. Whereas we prefer magnesium and calcium containing compounds, other alkaline earth metal compounds containing barium and strontium may also be used. We prefer that the catalytic alkaline earth metal com-
35 pounds should be soluble in the ester-interchange reaction mixture, such as alkaline earth metal salts of aliphatic and aromatic carboxylic acids, particularly those in which the substituents are of a polar nature. Preferred ester-interchange catalysts include
40 magnesium carbonate, magnesium oxide and calcium acetate. If desired an additional ester-interchange catalyst may be used in conjunction with the alkaline earth metal
45 compounds, for example cobalt acetate.

As stated in the process disclosed in British Patent Specification 802921, the amount of the phosphorous acid salt formed affects the degree of colour and/or of turbidity of the resultant polyester. For poly-
50 esters to be used in the manufacture of filaments, it is normally desirable that the whole of the alkaline earth metal compound present with ester-interchange product should
55 be converted to an alkaline earth metal salt of a phosphorous acid in order to be catalytically inert in the subsequent polycondensation reaction. However, it has been found that polyesters containing a small amount
60 of insoluble alkaline earth metal compounds can be converted to films having improved friction characteristics, thus by controlling the extent of formation of phosphorus acid salts in the polyester to be converted into
65 film, the frictional properties of the film

can be adjusted.

Any phosphorus compound may be added to the polyester forming reactants which permits an alkaline earth metal salt of an acid of phosphorus to be present during the
70 polycondensation reaction. Suitable phosphorus compounds to be added include phosphoric acid, phosphorus acid, alkyl phosphates and phosphites, aryl phosphates and phosphites, ammonium phosphates and
75 phosphites and glycol phosphates and phosphites. Our preferred phosphorus compounds are the trivalent compounds of phosphorus, particularly phosphorus acid and triphenyl phosphite.
80

As the pentavalent antimony compounds to be used as the polycondensation catalysts in the process of our invention, we prefer to use antimony pentoxide or antimonious acid
85 but other pentavalent antimony compounds such as organic antimonates, for example pentaethyl antimonate or antimony pentaglycoloxide may be used readily. As commercially obtained, some so-called penta-
90 valent antimony compounds often contain small amounts of trivalent antimony compounds, commonly as the trioxide and in order to obtain the best results the pentavalent antimony compound should contain
95 less than 1% preferably less than 0.5% by weight of a trivalent antimony compound.

Of the many catalytic combinations which can be used according to the process of our invention we prefer to use a catalytic mag-
100 nesium or calcium compound, triphenyl phosphite or phosphorus acid and antimonious acid or antimony pentoxide. These preferred catalytic combinations have been found to give polyesters having the highest degrees of
105 luminance consistent with minimum degrees of yellowness.

The ester-interchange catalyst may be added in any amount such that it does not cause undesirable coloration in the final
110 polyester, but in practice we have found it preferable to add the catalytic alkaline earth metal compound in an amount between 0.01-0.2% by weight based on the weight of dialkyl terephthalate used.

The phosphorus compound added to in-
115 activate the ester-interchange catalyst is normally added in an amount up to the stoichiometric equivalent of the weight of ester-interchange catalyst according to the degree of inactivation desired. However, if
120 desired, a total greater than a stoichiometric equivalent may be added, and this excess may be added either at then end of the ester-interchange or during the polycondensation reaction itself.
125

The pentavalent antimony compound used as polycondensation catalyst can also be added in any suitable amount provided that it does not cause undesirable coloration
130 of the final polyester. We prefer that the

polycondensation catalyst be added in an amount between 0.005 and 0.1% by weight based on the original weight of dialkyl terephthalate used. The polycondensation catalyst may be usually added to the ester-interchange reaction mixture if desired, but we have found that it is preferable to add the polycondensation catalyst after inactivation of the ester-interchange catalyst has taken place. This later addition results in the obtaining of polyesters having remarkably high degrees of luminance and low degrees of yellowness. In the case of certain polycondensation catalysts such as antimony pentafluoride, it is essential that they be added after ester-interchange as the presence of the fluoride ion in the reaction mixture inhibits the ester-interchange.

Both the ester-interchange and polycondensation reactions may take place at atmospheric or under sub- or super-atmospheric pressure conditions, in either the liquid or solid phase. We prefer that the ester-interchange takes place under atmospheric pressure conditions at a temperature between 150 and 235°C and that polycondensation takes place under reduced pressure conditions preferably at a pressure less than 1 mm. of mercury in the temperature range of 210-300°C., desirably below 285°C., preferably in the liquid, i.e. melt phase.

During ester-interchange methanol is continuously withdrawn from the reactor and when methanol ceases to be evolved, the ester-interchange is substantially complete. Reduced pressure is essential during the polycondensation stage for the satisfactory removal of the glycol liberated, to enable the formation of a high molecular weight polyalkylene terephthalate from which filaments and films can be drawn.

The present invention is particularly exemplified hereinafter with respect to the preparation of polyethylene terephthalate from dimethyl terephthalate and ethylene glycol; however it should be understood that the process is fully applicable to the manufacture of filament and film-forming polyesters in which the starting materials may be any lower alkyl ester of terephthalic acid or mixture of such esters or these esters may be partially replaced, e.g. up to 40% by weight with esters of other dicarboxylic acids such as of isophthalic, phthalic, adipic, sebacic, glutaric and naphthalic acids. Alternatively glycols other than ethylene glycol, of the series $\text{HO}(\text{CH}_2)_n\text{OH}$ where $n=2-10$ inclusive, may be used or mixtures of any of these glycols with one another or with other glycols such as hexahydro-paraxylene glycol may also be used as starting materials.

The process of our invention while exemplified as a batch process may readily be operated as a continuous process in either or both of the ester-interchange and polycon-

densation stages. The catalyst of our invention may be added to the reaction mixture when operating continuously either individually, collectively or in the form of a solution or a dispersion, for example in an alcohol and for this we have found the use of the glycol used in the reaction to be a particularly suitable solvent or dispersing agent for the catalysts.

For the purpose of comparing the yellowness and luminance of samples of polyester the reflectance of polymer and in the form of ribbon may be measured on a "Color-master" which is the trade name for the differential colorimeter manufactured by the Manufacturers Engineering and Equipment Corporation.

Luminance (Y on the C.I.E. system) is a measure of the proportion of the incident light reflected and yellowness is a measure, based on C.I.E. chromaticity co-ordinates, of the separation of the point representing the colour rating of the polymer from the point representing standard illuminant 'C', positive values being measured in the direction of a dominant wave-length of 580-590 mμ and negative values in the direction of a dominant wave-length of 470-490 mμ.

Relatively small variations in the luminance and yellowness values of polyesters prepared for filament and film ultimate end uses can be of considerable importance in deciding the value of such polyesters for commercial purposes and it is thus essential, particularly for filament end uses, that such polyesters should have high degrees of luminance together with low degrees of yellowness.

The improved colour of polyesters obtained using the process of the present invention is shown to be particular to the catalytic system used for when the antimony trioxide in the prior art catalyst system, as disclosed in United States Patent Specification 2650213, that is a litharge/triphenyl phosphite/antimony trioxide system, is replaced by a pentavalent antimony compound, for example antimony pentoxide no decrease in yellowness occurs with no useful increase of luminance.

We have found that when the yellowness value is not substantially less than zero and when using a tri- or penta-valent antimony compound as the polycondensation catalyst, a useful criterion of colour is obtained by subtracting the yellowness value from that of the luminance. The best colour is obtained when the luminance value minus the yellowness value is at a maximum. However, for a comparison of this type to be made it is essential that the polyesters in the Examples to be compared are manufactured under identical conditions for example on the same scale and in the same equipment. It must be also noted that no direct com-

parison using this criterion can be made if an additional ester-interchange catalyst is present in the ester-interchange reaction mixture as this catalyst in itself may upset the luminance/yellowness balance.

The following Examples, in which all parts are by weight, illustrate but do not limit the scope of our invention.

EXAMPLE 1

10 Dimethyl terephthalate (100 parts), ethylene glycol (70.5 parts), magnesium carbonate (0.03 parts) and antimony acid (0.05 parts) were heated at 170-230°C until the theoretical amount of methanol for complete ester-interchange had been collected. 15 Phosphorus acid (0.03 parts) was added. The excess glycol was distilled off, and the pressure was gradually reduced to 0.5 mm. Polymerisation was continued at a temperature of 280°C until an intrinsic viscosity of 0.70 had been attained, when the polymer was extruded. The product was colourless.

By comparison with the above, Example 1 was again carried out, but without the addition of phosphorus acid, the product was pale yellow in appearance.

EXAMPLE 2

(a) Dimethyl terephthalate (100 parts), ethylene glycol (68 parts) and magnesium carbonate (0.035 parts) were heated together in an agitated stainless steel vessel. Evolution on methanol commenced at a temperature of 175°, and continued for 1 hr. 45 min. until the theoretical yield of methanol (40 parts) had been evolved. The temperature was then 225°C. Glycol (20 parts) was then distilled off, and the residue was transferred into a second stainless steel vessel, also agitated. Phosphorus acid (0.035 part) was added, followed after an interval of 5 minutes by fine slurries of antimony pentoxide (0.045 part) and titanium dioxide (0.05 part) in glycol. The pressure was reduced and the temperature raised until a pressure of 0.2 mm. of mercury and a temperature of 280° had been attained. The desired degree of polymerisation was reached after 2 hr. 20 min. at a pressure below 1 mm., and the polymer was extruded and cast as a ribbon on water-cooled rollers.

The reflectance of the polymer ribbon was measured on a "Colormaster"; the luminance was 77 and the yellowness 11.

(b) Polymer made in the same equipment and under the same conditions, but with the addition of 0.01 part of cobalt carbonate together with the magnesium carbonate, gave a luminance of 65 and a yellowness of -1.

(c) Dimethyl terephthalate (100 parts), ethylene glycol (68 parts), magnesium carbonate (0.035 part), and antimony trioxide (0.04 part) were heated together in an agitated stainless steel vessel. Evolution of methanol commenced at a temperature of 175°, and continued for 1 hr. 55 min. until

the theoretical yield of methanol (40 parts) had been evolved. The temperature was then 225°C. Glycol (20 parts) was distilled off, and the residue was transferred into a second stainless steel autoclave, also agitated. Phosphorus acid (0.035 part) was added, followed after 5 minutes by a fine slurry of titanium dioxide (0.5 part) in glycol. The pressure was reduced and the temperature raised until a pressure of 0.3 mm. of mercury and temperature of 280° had been attained. The desired degree of polymerisation was reached after 2 hr. at a pressure below 1 mm., and the polymer was extruded and cast as a ribbon on water-cooled rollers.

The ribbon had a luminance of 56 and a yellowness of 4. The luminance using antimony pentoxide was therefore 21 units better than with the trioxide and the yellowness only 7 units higher.

EXAMPLE 3

Polyethylene terephthalate was made according to the method described in Example 2, but instead of antimony pentoxide, antimony pentachloride (0.09 part) was added, and the titanium dioxide added as a delustrant was omitted. The resulting polymer was clear, bright and colourless.

The corresponding polymer made using antimony trioxide (0.04 part) was greenish-grey in appearance, owing to separation of a small amount of antimony during the course of the polycondensation. A similar pale green colour was obtained using antimony trioxide or potassium antimonyl tartrate as polycondensation catalyst in U.S. Patent No. 2,739,957.

EXAMPLE 4

Polyethylene terephthalate was made according to the method described in Example 2 but instead of antimony pentoxide, pentethyl antimonate (0.095 part) was added, and the titanium dioxide added as a delustrant was omitted. The polymerisation was normal, and the resulting polymer was clear, bright and colourless.

EXAMPLE 5

Polyethylene terephthalate was made according to the method described in Example 2, but instead of antimony pentoxide, antimony acid (0.052 part) was added. The resulting polymer ribbon had a luminance of 63 and a yellowness of 2. The luminance was therefore 7 units better, and the yellowness 2 units better than from the polymer made using antimony trioxide in Example 2. (c).

EXAMPLE 6

Polyethylene terephthalate was made according to the method described in Example 2 but using only 0.023 part of magnesium carbonate as ester interchange catalyst and adding 0.08 part of magnesium antimonate instead of the antimony pentoxide. The polymerisation was normal, and the resulting

polymer ribbon had a luminance of 65 and a yellowness of 3. The luminance was therefore 9 units and the yellowness 1 unit better than from the polymer made using antimony trioxide in Example 2 (c).

EXAMPLE 7

Polyethylene terephthalate was made according to the method of Example 2 (a), but with the addition of calcium acetate (0.07 part) instead of the magnesium carbonate. Methanol evolution commenced at 150°C, and continued for 1 hr. 45 min. until the theoretical yield of methanol had been evolved. Glycol removal and polycondensation were carried out as in Example 2 (a), and the resulting polymer ribbon had a luminance of 73 and a yellowness of 5.

Polymer made according to Example 2 (c) but with calcium acetate (0.07 part) instead of magnesium carbonate, had a luminance of 52 and a yellowness of 8. The luminance was therefore 21 units better and the yellowness 3 units better using antimony pentoxide than using antimony trioxide.

EXAMPLE 8

Polyethylene terephthalate was made according to method described in Example 2 except that the catalysts used were:—

Basic magnesium carbonate	0.035 part
Antimonic acid	0.05 part
Triphenyl phosphite	0.13 part

The magnesium carbonate was added before ester interchange, and the antimonic acid and triphenyl phosphite after ester interchange but before polymerisation.

The resulting polymer had a luminance of 68 and a yellowness of 1.

EXAMPLE 9

(a) Polyethylene terephthalate was made according to the method described in Example 8, except that the ester interchange stage was carried out in a glass vessel and the polymerisation temperature was 285° instead of 280°. Polymer of luminance 68 and yellowness 1 was obtained.

(b) Example 9a was repeated, but using calcium acetate (0.06 part) as ester interchange catalyst instead of magnesium carbonate. Polymer of luminance 71 and yellowness 3 was obtained.

(c) Example 9a was repeated, but using manganese acetate (0.02 part) as ester interchange catalyst instead of magnesium carbonate. Polymer of luminance 63 and yellowness -1 was obtained.

(d) Example 9a was repeated, but using cobalt acetate (0.02 part) as ester interchange catalyst instead of magnesium carbonate. Polymer of luminance 58 and yellowness -17 was obtained.

(e) Example 9a was repeated, but using zinc acetate (0.015 part) as ester interchange catalyst instead of magnesium carbonate. Polymer of luminance 68 and yellowness 6 was obtained.

EXAMPLE 10

Polyethylene terephthalate was made in the equipment used for Example 8, but using as catalysts litharge (0.02 part), antimony trioxide (0.05 part), and triphenyl phosphite (0.1 part), as described in Example I of U.S. Patent No. 2,650,213 except that 0.5 parts of titanium dioxide, as delustrant were also added. Ester interchange took 4 hr. 46 min., and polymerisation to the required intrinsic viscosity of 0.675 took 4 hr. 12 min. These times were longer than those required for Example 9a, whose ester interchange took 3 hr. 39 min. and polymerisation took 2 hr. 44 min. to the same intrinsic viscosity of 0.675. The polymer ribbon had a luminance of 68 and a yellowness of 7, respectively equal to and 6 units worse than the polymer prepared in Example 9a. By comparison, when the antimony trioxide was replaced by the pentoxide no decrease in yellowness occurred, the product having an intrinsic viscosity 0.646 and a luminance of 73 with a yellowness of 9.

EXAMPLE 11

Example 8 was repeated without the addition of triphenyl phosphite. Polymer of luminance 72 and yellowness 15 was obtained. The polymerisation time was 205 min., compared with 260 min., for the experiment described in Example 8. The omission of the triphenyl phosphite thus improved the polymerisation time but resulted in a deterioration in colour.

EXAMPLE 12

Example 8 was repeated, but using a solution of ethylene glycol phosphite (equivalent to 0.035 part of phosphorous acid) in glycol (2 parts) instead of triphenyl phosphite. Polymer of luminance 70 and yellowness 3 was obtained. The use of an aliphatic phosphite instead of an aryl phosphite thus had little effect on the colour of the polymer.

EXAMPLE 13

Example 8 was repeated using phosphorous acid (0.035 part) instead of triphenyl phosphite. Polymer of luminance 71 and yellowness 6 was obtained. The softening point of the polymer, measured by a penetrometer method on a crystallised sample, was 259.7°, compared with a softening point of 263.4° for the polymer prepared in Example 8.

Usually a pure polyethylene terephthalate is desired, and then it is preferable to use triphenyl phosphite, since a lower softening point indicates the presence of a small proportion of diethylene glycol units in the chain; on the other hand, the presence of these diethylene glycol units enhances the dye uptake of the resulting fibres, and this product may be useful where higher dye uptake is desired.

EXAMPLE 14

Pentaethyl antimonate was dissolved in ethylene glycol by warming. On standing in the absence of atmospheric moisture for a few hours the solution deposited colourless crystals which were centrifuged off, washed with dry methanol, and dried. Intra-red spectroscopic examination showed that the crystals were not pentaethyl antimonate but an ester formed with ethylene glycol, containing hydroxyethyl and probably also ethylenedioxy groups; chemical examination showed that the antimony was still in the pentavalent state. The product was therefore antimony pentaglycoloxide.

Polyethylene terephthalate was made according to the method described in Example 2, but instead of antimony pentoxide, antimony pentaglycoloxide (0.1 part) was added and the titanium dioxide was omitted. The resulting polymer was clear, bright and colourless.

The intrinsic viscosity of the polyesters obtained in the Examples enabled them to be readily converted to filaments and films having desirable properties, particularly as regards their absence of yellowness and their possession of high degrees of luminance.

Examples 15-19 were all undertaken on similar equipment to and under the condi-

tions used in Example 2. However in each case the percentage weight of ingredients used, based on the weight of dimethyl terephthalate were

Magnesium carbonate	0.035%	35
Antimonic acid	0.05%	
Triphenyl phosphite	0.13%	
Titanium dioxide	0.5%	

In each example the ester-interchange catalyst, magnesium carbonate, was added at the commencement of ester-interchange. The following table shows the points and order of addition of antimonic acid, triphenyl phosphite and titanium dioxide, together with the analytical data for the polymers obtained. Vacuum was applied when the batch temperature was 235°C and full vacuum was reached when the temperature had risen to 260-270°C. The final batch temperature was 280°C.

The progress of the polycondensation reaction was determined by measuring the power required to turn the agitator in the polyester melt. This was recorded in kilowatts at a constant voltage, the difference between the reading at the beginning of the polycondensation reaction and that at any particular point in the reaction being termed ΔP .

Ex- ample No.	Point of addition of			Polyconden- sation time (from application of full vacuum to stopping agitation)	Intrinsic Viscosity	Softening Point °C	Colour		
	Antimonic acid	Triphenyl phosphite	Titanium dioxide				Lumi- nance Value	Yellow- ness Value	L - Y
15	At 210°C to ester- interchange vessel	At 210°C to ester- interchange vessel 5 minutes after anti- monic acid	At 210°C to ester- interchange vessel 5 minutes after the triphenyl phosphite	2 hours 47 mins.	0.687	263.3	70	3	67
16	At 210°C to ester- interchange vessel, 5 minutes after the triphenyl phosphite	At 210°C to ester- interchange vessel	At 210°C to ester- interchange vessel 5 minutes after the antimonic acid	2 hours 26 mins.	0.676	263.5	70	3	67
17	At 210°C to ester- interchange vessel	Half charge at 210°C to ester- interchange vessel 5 minutes after anti- monic acid. Second half added at 280°C to polycondensation autoclave, 2 hours after full vacuum was reached	At 210°C to ester- interchange vessel 5 minutes after the triphenyl phosphite	3 hours 30 mins.	0.654	263.1	53	-9	62

Ex- ample No.	Point of addition of			Polyconden- sation time (from application of full vacuum to stopping agitation)	Intrinsic Viscosity	Softening Point °C	Colour		L-Y
	Antimonic Acid	Triphenyl phosphite	Titanium dioxide				Lumi- nance Value	Yellow- ness	
18	At 210°C to ester-interchange vessel	At 280°C to polycondensation autoclave, 1½ hours after full vacuum was reached	At 210°C to ester-interchange, 5 mins. after the antimonic acid	3 hours 5 mins.	0.688	260.7	46	-12	58
19	At 210°C to ester-interchange vessel	At 280°C to polyautoclave, 1 hour after full vacuum was reached	At 210°C to ester-interchange, 5 mins. after the antimonic acid	1 hour 8 mins.	0.684	260.3	58	5	53

In Example 17, in which half the triphenyl phosphite charge was added at 210°C. and half at 280°C and in Examples 18 and 19 in which the whole of the triphenyl phosphite was added at 280°C, the addition at 280°C was always made when 80% of the required rise in ΔP had taken place.

In Examples 17 and 18, the triphenyl phosphite was emulsified with 10 ml. glycol before addition at 280°C. Glycolysis caused a 10 fall in ΔP.

In Example 19 the triphenyl phosphite was added alone at 280°C. A very much smaller fall in ΔP was observed.

The above Examples 15-19 having been 15 undertaken under similar operating conditions may therefore be compared with each other.

Example 15, when compared with Example 16, shows that there is substantially 20 no difference in polyester colour and other resultant properties, whether the polycondensation catalyst is added immediately before or after the phosphorus compound addition. We prefer to add the polycondensation 25 catalyst, for example antimonic acid, before the phosphorus compound for example triphenyl phosphite; in order to assist the solubilisation of the polycondensation catalyst before polycondensation commences. This 30 preferred order of addition shows its advantage by a decreased polycondensation time.

Example 17, in which some of the phosphorus compound is added before polycondensation commences, shows that a polyester is obtained having improved colour over the polyesters obtained in Examples 18 and 19, where the phosphorus compound was added after a considerable degree of 40 polycondensation had taken place.

WHAT WE CLAIM IS:—

1. In a process for the manufacture of highly polymeric polymethylene terephthalates by reacting a dialkyl ester of terephthalic acid with a glycol of the series $\text{HO}(\text{CH}_2)_n\text{OH}$, where n is greater than 1 but not exceeding 10, in the presence of a catalytic amount of an alkaline earth metal compound and converting the alkaline earth 50 metal, prior to polycondensing the ester-interchange product, wholly or in part, to a phosphorus containing compound of that metal, which is catalytically inert, the improvement comprising polycondensing in the 55 presence of a catalytic amount of a pentavalent antimony compound.

2. A process according to Claim 1 wherein the alkaline earth metal compound used as the ester-interchange catalyst is a 60 compound of magnesium or calcium.

3. A process according to Claim 2 wherein magnesium carbonate is used.

4. A process according to Claim 2 wherein calcium acetate is used. 65

5. A process according to any of the

preceding claims wherein cobalt acetate is used as an additional ester-interchange catalyst.

6. A process according to any of the preceding claims wherein the weight of ester-interchange catalyst is 0.01-0.2% of the weight of dialkyl terephthalate used.

7. A process according to any of the preceding claims wherein the alkaline earth metal is converted to a phosphorus containing compound of that metal by the addition of a trivalent phosphorus compound to the ester-interchange reaction product.

8. A process according to Claim 7 wherein the trivalent phosphorus compound is tri-phenyl phosphite.

9. A process according to Claim 7 wherein the trivalent phosphorus compound is phosphorus acid.

10. A process according to any of the preceding claims wherein the alkaline earth metal is converted to a phosphorus containing compound of that metal by the addition of a phosphorus compound added, in an amount at least equal to the stoichiometric equivalent of the weight of ester-interchange catalyst present.

11. A process according to any of the preceding claims wherein the pentavalent antimony compound is present in an amount between 0.005 and 0.1% by weight based on the original weight of dialkyl terephthalate used.

12. A process according to any of the preceding claims wherein the pentavalent antimony compound is antimony pentoxide.

13. A process according to any one of the Claims 1-11 wherein the pentavalent antimony compound is antimononic acid.

14. A process according to any one of the Claims 1-11, wherein the pentavalent

antimony compound is an organic antimonate.

15. A process according to Claim 14, wherein the organic antimonate is pentamethyl antimonate.

16. A process according to Claim 14, wherein the organic antimonate is antimony pentaglycoloxide.

17. A process according to any of the preceding claims wherein the pentavalent antimony compound used contains less than 1%, preferably less than 0.5% by weight of an antimony compound in the trivalent state.

18. A process according to any of the preceding claims wherein the pentavalent antimony compound used is added to the reaction mixture after inactivation of the ester-interchange catalyst.

19. A process according to any of the preceding claims wherein the ester-interchange takes place at a temperature between 150 and 235°C.

20. A process according to any of the preceding claims wherein the polycondensation stage takes place under reduced pressure conditions in the temperature range of 210-300°C., preferably below 285°C.

21. A process for the manufacture of highly polymeric polymethylene terephthalates according to Claim 1 substantially as hereinbefore described with particular reference to the Examples.

22. Highly polymeric polymethylene terephthalates whenever made by a process claims in any of the preceding Claims.

23. Fibres and films wherever obtained from the highly polymeric polymethylene terephthalates as claimed in Claim 22.

ALFRED O. BALL,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

Manufacture of Highly Polymeric Polymethylene Terephthalates

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare this invention to be described in the following statement:—

This invention relates to the manufacture of polyesters, more particularly to fibre-forming polyesters obtained from terephthalic acid.

In U.S. Patent 2,739,957 there is claimed an improved process for the manufacture of filament and film-forming polyethylene terephthalate wherein ethylene glycol is reacted under ester-interchange conditions with an alkyl ester of terephthalic acid and a saturated aliphatic monohydric alcohol containing from 1-4 carbon atoms and the resulting glycol terephthalate is polymerised, the improvement which comprises carrying out the ester-interchange reaction in the pre-

sence of a catalyst comprising essentially at least one calcium compound and carrying out the polymerisation reaction in the presence of a catalyst consisting of at least one calcium compound and at least one antimony compound. In the specification of this patent it is stated that "the preferred antimony compounds are the colourless or white compounds in which antimony exhibits the valence of three".

It is also known from British Patent 802,921 to produce highly polymeric polymethylene terephthalates by reacting a dialkyl ester of terephthalic acid with a glycol of the series $\text{HO}(\text{CH}_2)_n\text{OH}$, where n is greater than 1 but not exceeding 10, in the presence of an alkaline earth metal compound and the product is then subjected to polycondensation in the presence of a catalyst, characterised in that the alkaline earth

metal is converted, wholly or in part, to a phosphorus acid salt of that metal which is catalytically inert and which is soluble in the polycondensation reaction mixture and in the final polyester.

Of the prior art polycondensation catalysts in the manufacture of fibre-forming polyesters the normally preferred catalyst has been antimony trioxide and this catalyst has been used in the commercial manufacture of polyethylene terephthalate.

We have now found that if a functional derivative of terephthalic acid is reacted with a glycol or a functional derivative thereof in the presence of a catalyst and that if this catalyst is inactivated after the ester-interchange reaction has been completed, by the addition of a phosphorus compound and the product thus obtained is polycondensed in the presence of a pentavalent antimony compound, the resulting fibre and filament-forming polyester is of superior colour to that using a trivalent antimony compound, whether the ester-interchange catalyst has been inactivated by the addition of a phosphorus compound or not.

According to the present invention we provide a process for the manufacture of fibre and film-forming polyesters by reacting a glycol or a functional derivative thereof with a functional derivative of terephthalic acid, preferably dimethyl terephthalate, in the presence of an ester-interchange catalyst, preferably inactivating the catalyst after ester-interchanging by adding phosphorus compound and polycondensing the ester-interchange product, characterised in that the polycondensation reaction takes place in the presence of a pentavalent compound of antimony.

Our preferred pentavalent antimony compounds are antimoninic acid, salts and esters of antimoninic acid, and antimony pentoxide. As the glycol we prefer to use ethylene glycol, but any glycol of the series $\text{HO}(\text{CH}_2)_n\text{OH}$, where $n=2-10$ inclusive may be used if desired, or one can use other suitable diols such as 1:4 dihydroxymethyl cyclohexane or mixtures of these compounds may also be used.

If desired the terephthalic acid functional derivative may be partially replaced by the functional derivative of another dicarboxylic acid such as isophthalic, succinic or sebacic acids.

As ester-interchange catalysts any of the catalysts of the prior art may be used but our preferred catalysts are compounds of magnesium, for example, magnesium carbonate or of zinc, for example, zinc acetate or of manganese, for example manganous acetate, or of calcium, for example calcium acetate, or of cobalt, for example, cobalt acetate.

It has been found that polyethylene tere-

phthalate prepared by a process using the catalyst system of the present invention shows a lower degree of yellowness as compared with polyethylene terephthalate prepared using catalyst systems of the prior art having an equal degree of luminance. In polyesters, manufactured for film and fibre-forming purposes, it is desirable that the degree of luminance is as high as possible and the yellowness is about 0 or even slightly negative when measured in the manner described in the Examples.

The following Examples, in which all parts and percentages are by weight, illustrate but do not limit the scope of our invention.

Example 1.

(a) Dimethyl terephthalate (100 parts), ethylene glycol (68 parts), and magnesium carbonate (0.035 parts) were heated together in an agitated stainless steel vessel. Evolution of methanol commenced at a temperature of 175° , and continued for 1 hr. 45 min. until the theoretical yield of methanol (40 parts) had been evolved. The temperature was then 225° . Glycol (20 parts) was then distilled off, and the residue was transferred into a second stainless steel vessel, also agitated. Phosphorous acid (0.035 part) was added, followed after an interval of 5 minutes by fine slurries of antimony pentoxide (0.045 part) and titanium dioxide (0.5 part) in glycol. The pressure was reduced and the temperature raised until a pressure of 0.2 mm. of mercury and a temperature of 280° had been attained. The desired degree of polymerisation was reached after 2 hr. 20 min. at a pressure below 1 mm., and the polymer was extruded and cast as a ribbon on water-cooled rollers.

The reflectance of the polymer ribbon was measured on a "Colormaster", the luminance was 77 and the yellowness 11. Luminance is a measure of (Y on the C.I.E. system) the proportion of the incident light reflected, and yellowness is a measure, based on C.I.E. chromaticity co-ordinates, of the separation of the point representing the colour rating of the polymer from the point representing standard illuminant 'C', positive values being measured in the direction of a dominant wave-length of 580-590 $m\mu$ and negative values in the direction of a dominant wave length of 470-490 $m\mu$.

(b) Polymer made in the same equipment and under the same conditions, but with the addition of 0.01 part of cobalt carbonate together with the magnesium carbonate, gave a luminance of 65 and a yellowness of -1.

(c) Dimethyl terephthalate (100 parts), ethylene glycol (68 parts), magnesium carbonate (0.035 part), and antimony trioxide (0.04 part) were heated together in an agitated stainless steel vessel. Evolution of methanol commenced at a temperature of 130

175°, and continued for 1 hr. 55 min. until the theoretical yield of methanol (40 parts) had been evolved. The temperature was then 225°. Glycol (20 parts) was distilled off, and the residue was transferred into a second stainless steel autoclave, also agitated. Phosphorous acid (0.035 part) was added, followed after 5 minutes by a fine slurry of titanium dioxide (0.5 part) in glycol. The pressure was reduced and the temperature raised until a pressure of 0.3 mm of mercury and temperature of 280° had been attained. The desired degree of polymerisation was reached after 2 hr. at a pressure below 1 mm., and the polymer was extruded and cast as a ribbon on water-cooled rollers.

The ribbon had a luminance of 56 and a yellowness of 4. The luminance using antimony pentoxide was therefore 21 units better than with the trioxide, and the yellowness only 7 units higher.

Example 2

Polyethylene terephthalate was made according to the method described in Example 1, but instead of antimony pentoxide, antimony pentachloride (0.09 part) was added, and the titanium dioxide added as a delustrant was omitted. The resulting polymer was clear, bright and colourless.

The corresponding polymer made using antimony trioxide (0.04 part) was greenish-grey in appearance, owing to separation of a small amount of antimony during the course of the polycondensation. A similar pale green colour was obtained using antimony trioxide or potassium antimonyl tartrate as polycondensation catalyst in U.S. Patent No. 2,739,957.

Example 3

Polyethylene terephthalate was made according to the method described in Example 1, but instead of antimony pentoxide, pentamethyl antimonate (0.095 part) was added, and the titanium dioxide added as a delustrant was omitted. The polymerisation was normal, and the resulting polymer was clear, bright and colourless.

Example 4

Polyethylene terephthalate was made according to the method described in Example 1, but instead of antimony pentoxide, antimoninic acid (0.052 part) was added. The resulting polymer ribbon had a luminance of 63 and a yellowness of 2. The luminance was therefore 7 units better, and the yellowness 2 units better than from the polymer made using antimony trioxide in Example 1 (b.).

Example 5

Polyethylene terephthalate was made according to the method described in Example 1, but using only 0.023 part of magnesium carbonate as ester interchange catalyst and adding 0.08 part of magnesium antimonate instead of the antimony pentoxide. The polymerisation was normal, and the resulting polymer ribbon had a luminance of 65 and a yellowness of 3. The luminance was therefore 9 units and the yellowness 1 unit better than from the polymer made using antimony trioxide in Example 1 (c.).

Example 6

Polyethylene terephthalate was made according to the method of Example 1 (a), but with the addition of calcium acetate (0.07 part) instead of the magnesium carbonate. Methanol evolution commenced at 150°, and continued for 1 hr. 45 min. until the theoretical yield of methanol had been evolved. Glycol removal and polycondensation were carried out as in Example 1 (a), and the resulting polymer ribbon had a luminance of 73 and a yellowness of 5.

Polymer made according to Example 1 (c.) but with calcium acetate (0.07 part) instead of magnesium carbonate, had a luminance of 52 and a yellowness of 8. The luminance was therefore 21 units better and the yellowness 3 units better using antimony pentoxide than using antimony trioxide.

The name 'Colormaster' is the trade name for the differential colorimeter manufactured by the Manufacturers Engineering and Equipment Corporation.

ALFRED O. BALL.
Agent for the Applicants.

PROVISIONAL SPECIFICATION

Manufacture of Highly Polymeric Polymethylene Terephthalates

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare this invention to be described in the following statement:—

This invention relates to the manufacture of highly polymeric polymethylene terephthalates, more particularly to a catalyst system which permits the manufacture of substantially colourless polyesters.

It is known, for example, from U.S.P. 2,465,319 to react dimethyl terephthalate with ethylene glycol in the presence of mag-

nesium oxide to form bis-beta-hydroxyethyl terephthalate, which is then polycondensed to give fibre-forming polyethylene terephthalate.

Polyethylene terephthalate made using this catalyst system is inferior to that using many other ester-interchange catalysts, particularly as regards the colour of the polyester which in fibre form appears to be markedly yellow. The rate of polycondensation during the manufacture of the polyester is slow and this catalyst system is therefore not suitable as an economic commercial

method for producing polyethylene terephthalate.

In order to speed up the rate of polycondensation it is known to add a polycondensation catalyst, but the use of even the preferred polycondensation catalysts, for example, antimony compounds, causes some deterioration in the colour of the resulting polyester using a magnesium compound as the ester-interchange catalyst.

We have found that if a magnesium compound soluble in the ester-interchange reaction mixture is used as the ester-interchange catalyst and a phosphorus compound from the group comprising phosphoric acid, phosphorous acid, alkyl, aryl and ammonium phosphates and phosphites is added to the ester-interchange product before polycondensing in the presence of a polycondensation catalyst, such as antimony oxide, polycondensation proceeds at an economic rate and the resulting polyester is substantially colourless and from it fibres and films of very desirable colour can be produced.

According to the present invention we provide a process for the manufacture of fibre and film-forming polyesters, containing at least a major proportion of a highly polymeric polymethylene terephthalate by ester-interchanging a glycol of the series $\text{HO}(\text{CH}_2)_n\text{OH}$, wherein $n=2-10$ inclusive, with a functional derivative of terephthalic acid, preferably dimethyl terephthalate and polycondensing the ester-interchange product, characterised in that the ester-interchange takes place in the presence of a magnesium compound soluble in the ester-interchange reaction mixture and that a phosphorus compound, being a member of the group comprising phosphoric acid, phosphorous acid, alkyl phosphates, aryl phosphates, alkyl phosphites, aryl phosphites, ammonium phosphates, ammonium phosphites, is added to the ester-interchange product before polycondensing in the presence of an added polycondensation catalyst.

We prefer that a stoichiometric proportion of the phosphorus compound is added at the end of the ester-interchange sufficient to inactivate the catalytic metal used as the ester-interchange catalyst.

As the polycondensation catalyst we pre-

fer to use an antimony compound, such as the trioxide, fluoride or antimonious acid, as these antimony compounds produce no undesirable colour in the resulting polyester.

As the magnesium compound for use as the ester-interchange catalyst, we prefer to add magnesium carbonate, but other magnesium compounds, for example, salts of acids having a dissociation constant less than 10^{-3} can be used, provided they dissolve in the reaction mixture under the ester-interchange conditions to give a soluble magnesium compound which need not be the compound originally added, for example, magnesium glycoloxide. Magnesium oxide is also suitable and even magnesium metal may be used.

If desired, a delustrant, for example, titanium dioxide may also be added to the polyester-forming mixture.

The following Examples, in which all parts and percentages are by weight, illustrate but do not limit the scope of our invention. These Examples (listed numerically) are shown in comparison with Examples (listed alphabetically) where no phosphorus compound is added and/or no additional polycondensation catalyst is present during the polycondensation stage.

The following ester-interchange and polycondensation reactions were carried out under identical conditions. In each case 120 parts of highly purified dimethyl terephthalate and 97 parts of highly purified ethylene glycol were charged into a flask together with the ester-interchange and polycondensation catalysts, and heated until the theoretical amount of methanol had been evolved. The ester-interchange product was charged, together with the inactivating agent when used, to a polymerisation tube, free glycol was distilled off, and the residue was polymerised at a pressure of 0.005–0.2 mm. with a slow bleed of nitrogen through the molten mass for two hours. The intrinsic viscosity thus obtained gave a measure of the rate of polycondensation. The optical density of a 10% w/v solution of the polymer in dichloroacetic acid, measured at a wavelength of 400 $\text{m}\mu$ is a measure of the colour of the polymer.

Example	Catalyst System	Inactivating Agent	Intrinsic Viscosity	Optical Density of 10% solution at 400 m μ
5 1	Magnesium carbonate 0.035% Antimony trioxide 0.04%	Phosphorous acid 0.035%	0.57	0.08
10 2	Magnesium carbonate 0.035% Antimony trioxide 0.04%	Phosphoric acid 0.04%	0.59	0.13
A	Magnesium carbonate 0.04%	—	0.48	0.36
15 B	Magnesium carbonate 0.035% Antimony trioxide 0.04%	—	0.69	0.40

EXAMPLE 3

20 Dimethyl terephthalate (100 parts), ethylene glycol (70.5 parts) magnesium carbonate (0.03 parts) and antimony acid (0.05 parts) were heated at 170-230°C until the theoretical amount of methanol for complete ester-interchange had been collected. Phosphorous acid (0.03 parts) was added. The excess glycol was distilled off, and the pressure was gradually reduced to 0.5 mm. Polymerisation was continued at a temperature of 280°C until an intrinsic viscosity of 0.70 had been attained, when the polymer was extruded. The product was colourless.

EXAMPLE C

Example 3 was again carried out, but without the addition of phosphorous acid. The product was pale yellow in appearance

EXAMPLE 4

Dimethyl terephthalate (100 parts), ethylene glycol (70.5 parts), and magnesium carbonate (0.035 parts) were heated at 170-230°C until the theoretical amount of methanol for complete ester-interchange had been collected. Antimony trifluoride (0.05 parts) and phosphorous acid (0.024 parts) were added, followed by titanium dioxide (0.5%) as delustrant. Excess glycol was distilled off, and the pressure was gradually reduced to 0.5 mm. Polymerisation was continued at a temperature of 280°C until an intrinsic viscosity of 0.67 had been attained,

when the polymer was extruded.

EXAMPLE D

Example 4 was again carried out but without addition of phosphorous acid. The product using phosphorous acid appeared very much less yellow. The products of Examples 4 and D were spun and drawn under identical conditions. The fibre from the polymer using phosphorous acid was much more attractive in appearance than that without phosphorous acid.

Thus it can be seen that the catalyst system of the present invention permits the manufacture of polyethylene terephthalate at an economic polycondensation rate, resulting in a polyester of low optical density, as compared with polyesters obtained in the absence of phosphorus compounds using a magnesium compound as the ester-interchange catalyst. Furthermore, the polyester produced by the process of our present invention compares favourably with preferred catalyst systems of the prior art. For Example, U.S.P. 2,739,957 claims carrying out the ester-interchange reaction in the presence of a catalyst comprising essentially at least one calcium compound and carrying out the polymerisation reaction in the presence of a catalyst consisting of at least one calcium compound and at least one antimony compound. However, the polyester thus obtained although having only a very pale green tint is cloudy in appearance due to the insolubility of the calcium compound present in

the final polyester.

It has also been proposed in U.S.P.
2,650,213 to carry out the polymerisation re-
action in the presence of a catalyst system
5 consisting of litharge, antimony trioxide and

triphenyl phosphite. The polyester thus ob-
tained is very much inferior in colour.

ALFRED O. BALL,
Agent for the Applicants.

Berwick-upon-Tweed: Printed for Her Majesty's Stationery Office, by The Tweeddale Press Ltd.—1961
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may
be obtained.